

Ion Beam Synthesis, Microstructure, and Optical Properties of GaAsN Nanostructures

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ABSTRACT

We have investigated the ion beam synthesis, microstructure, and optical properties of GaAsN nanostructures. Transmission electron microscopy indicates the formation of crystalline nanostructures with lattice parameters close to those of pure cubic GaN. These nanostructures exhibit significant photoluminescence in the near infrared range. The apparent lowering of the fundamental band gap may be due to the incorporation of a small amount of As in GaN.

1. Introduction

Due to its tunable band gap in the near-infrared and simultaneous lattice-matching with GaAs, GaInNAs has recently emerged as a very promising candidate for the third junction in a high performance multi-junction solar cell [1]. To date, only a few percent N has been incorporated into nitride-arsenide structures synthesized by conventional epitaxial methods. An alternative approach is to implant nitrogen into III-As compounds, followed by an appropriate annealing sequence [2,3]. At present, the relationship between the microstructure and optical properties of ion beam synthesized nitride-arsenide structures remains unexplored. In this paper, we present a correlation between the microstructure and optical properties of nitride-arsenide nanostructures synthesized by nitrogen ion implantation into epitaxial GaAs, followed by rapid thermal annealing.

2. Experiment

For these investigations, $\sim 2 \mu\text{m}$ thick epitaxial GaAs films grown on (001) GaAs were implanted with 100 keV nitrogen ions using a dose of $5 \times 10^{17} \text{ cm}^{-2}$. During implantation, the substrate temperature was maintained at 300°C. Some of the implanted samples were subsequently rapid thermal annealed at 750, 800, or 850°C for 30 seconds. A retained nitrogen dose of $\sim 3 \times 10^{17} \text{ cm}^{-2}$ was confirmed via nuclear reaction analysis using the reaction $^{14}\text{N}(\text{d},\alpha)^{12}\text{C}$ [4]. TEM imaging and electron diffraction were carried out in a JEOL 4000EX operating at 400kV and a JEOL 2010FX operating at 200kV.

3. Results and Discussion

Fig. 1 shows dark field TEM images and corresponding selected area diffraction patterns of as-implanted and 750°C annealed samples. Both images show evidence of highly damaged (1) surface and (3) near-substrate regions surrounding a (2) $\sim 150 \text{ nm}$ middle layer. For the as-implanted sample shown in Fig. 1 (a), the middle layer

appears opaque, suggesting that it is amorphous. This is also indicated by the selected area diffraction (SAD) pattern shown in Fig. 1 (b), which contains both diffraction spots associated with cubic GaAs, and a diffuse ring presumably due to the amorphous layer. For the 750°C annealed sample shown in Fig. 1 (c), the middle layer contains a high density of bright dots, suggesting the formation of small crystallites. The corresponding SAD pattern in Fig. 1 (d) contains the cubic GaAs spots and the diffuse ring, plus additional rings due to crystalline regions with various orientations. Indexing of the diffraction pattern suggests the presence of cubic crystallites with a lattice parameter of 4.501 \AA , similar to that of pure cubic GaN [5]. It is interesting to note that the GaN-rich nanocrystals have apparently chosen to nucleate in the cubic form in a seemingly amorphous matrix, even though the wurtzite form of GaN is most stable thermodynamically [6]. This suggests that the seemingly amorphous matrix may possess some short-range order. In particular, it is likely that the majority of atoms retain their tetrahedral coordination, and some of them may act as the crystal nucleation site. Indeed, evidence of such short-range order has been found in GaAs amorphized by Ga and As co-implantation [7].

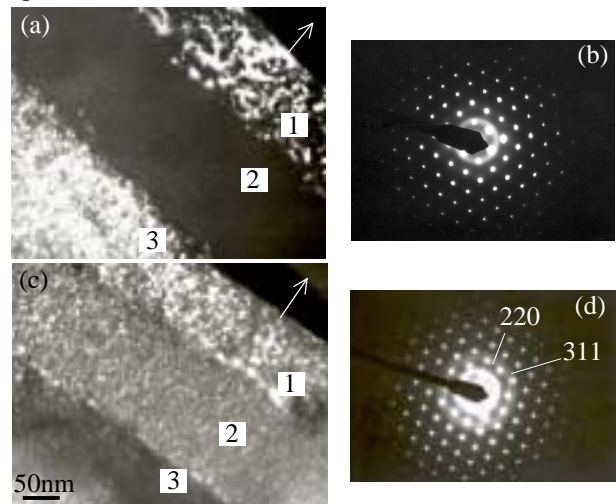


Fig. 1: Dark field TEM images of (a) as-implanted sample and (c) sample annealed at 750°C. (b) and (d) are the SAD patterns corresponding to (a) and (c), respectively.

Fig. 2 shows a HRTEM image of the middle layer of a sample rapid thermal annealed at 800°C. Crystallites with diameters of $\sim 5\text{-}10 \text{ nm}$, in an apparently amorphous matrix are evident. For the 750°C annealed sample, most of the nanostructures are smaller than 5 nm, while for the 850°C

annealed sample, the nanostructure diameters range from 10 to 20 nm.

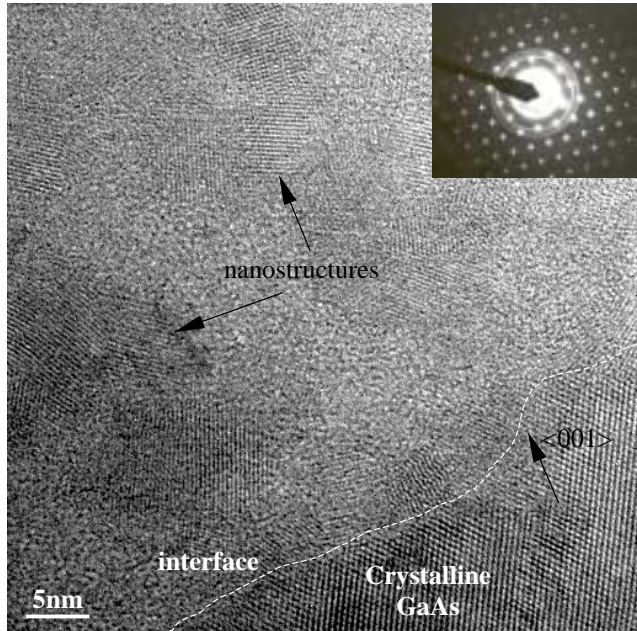


Fig. 2: HRTEM image and corresponding SAD pattern for the sample annealed at 800°C. The zone axis is $\langle 110 \rangle$.

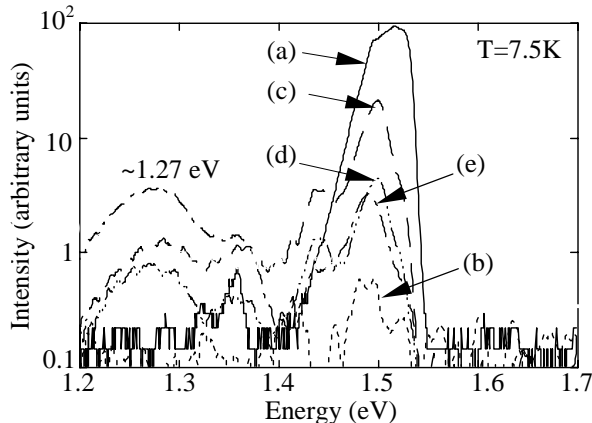


Fig. 3: Photoluminescence spectroscopy of the (a) unimplanted, (b) as-implanted, (c) 750°C annealed, (d) 800°C annealed, and (e) 850°C annealed samples.

Fig. 3 shows photoluminescence spectra of (a) unimplanted, (b) as-implanted, and (c)-(e) implanted plus annealed samples. In addition to the ~ 1.5 eV emission associated with GaAs present in all of the samples, an emission at ~ 1.27 eV is apparent in the annealed samples. Similar emissions near 1.3 eV, observed in earlier ion beam synthesis studies, were attributed to the formation of low nitrogen content $\text{GaAs}_{1-x}\text{N}_x$ alloys (with $x \sim 0.018$) [3]. However, in those studies, the microstructure of the samples was apparently not investigated and therefore, the existence of the As-rich GaAsN alloys was not confirmed. Our studies suggest instead that this emission is related to the formation of GaN-rich nanostructures. Preliminary depth-dependent cathodoluminescence spectroscopy measurements also support this conclusion [8]. It is interesting to note that the band gap energy (~ 1.27 eV) of

these GaN-rich nanostructures is significantly smaller than that of the bulk cubic GaN (~ 3.3 eV [9]). The incorporation of ~ 4 at% As into GaN is predicted to lower the bandgap to ~ 1.27 eV [10]. Using a linear interpolation of GaAs and GaN lattice parameters, this corresponds to an alloy, $\text{GaAs}_{0.08}\text{N}_{0.92}$, with a lattice parameter of ~ 4.59 Å, within 2.0% of our electron diffraction results.

4. Conclusions

In summary, we have synthesized GaN-rich nanostructures by nitrogen ion implantation into epitaxial GaAs films and subsequent rapid thermal annealing. These nanostructures possess symmetry and lattice parameters similar to that of cubic GaN. Photoluminescence spectroscopy shows a significant emission at ~ 1.27 eV for the implanted plus annealed samples, apparently related to the GaN-rich nanostructures. The lowering of the fundamental band gap of these nanostructures may be due to the incorporation of As into GaN.

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